

# Changing the Magnetic Configurations of Nanoclusters Atom-by-Atom

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The Korringa-Kohn-Rostoker Green (KKR) function method for non-collinear magnetic structures was applied on Mn and Cr ad-clusters deposited on the Ni(111) surface. By considering various dimers, trimers and tetramers, a large amount of collinear and non-collinear magnetic structures is obtained. Typically all compact clusters have very small total moments, while the more open structures exhibit sizeable total moments, which is a result of the complex frustration mechanism in these systems. Thus, as the motion of a single adatom changes the cluster structure from compact to open and vice versa, this can be considered as a magnetic switch, which via the local exchange field of the adatom allows to switch the cluster moment on and off, and which might be useful for future nanosize information storage.

## I. INTRODUCTION

Future technologies will be based on the magnetic properties of nanostructures. Such magnetic structures can be composed of magnetic atoms in precise arrangements. The magnetic properties of each atom can be profoundly influenced by its local environment. Recently, Gambardella *et al.*<sup>1</sup> showed that Co adatoms on Pt(111) have giant magnetic anisotropy energy (MAE) which may open the way to very high data storage densities. Indeed, clusters have the potential of increasing the density in information storage. One may envision that future magnetic hard discs with information carried by magnetic clusters, will have a storage density two orders of magnitude larger than those used today. Here we show, for elements without high MAE, *e.g.*, adatoms with half-filled 3d shells (Cr and Mn), that the magnetic properties due to the competition of antiferromagnetic (AF) exchange coupling may be used to switch the moment configuration in small ad-clusters. This may help reaching an important goal for magnet's technological relevance *e.g.* the ability of a magnet to store bits of 0 and 1 and being stable against thermal fluctuations. The bit 0 can be considered when no (or very small) magnetic moment is measured while high magnetic moment of the cluster can be considered as 1. In fact, five years ago, Jamneala *et al.*<sup>2</sup> investigated by STM Cr trimers deposited on Cu(111). They show that moving a Cr adatom of a compact trimer leads to a switching from the Kondo state to a magnetic one.

Magnetic excitations may degrade the performance of high-density memories. Indeed, Heinrich *et al.*<sup>3</sup> could elucidate the spin-flip of individual magnetic atoms that are dispersed on a non-magnetic matrix using scanning tunneling microscopy (STM). In the present paper, we propose to use the exchange field created by an adatom to switch the magnetic configuration of an ad-cluster from one magnetic state to another one.

Recently, there has been increasing interest in investigating non-collinear nanostructures on ferromagnetic<sup>4,5,6</sup> or non-magnetic surfaces<sup>7,8,9,10,11</sup>. Here, we choose as a substrate a ferromagnetic (FM) *fcc*-Ni surface which provides a magnetic coupling between the adatoms and

the substrate atoms. The Ni(111) surface was chosen, in which the surface geometry is triangular, meaning, in terms of magnetic coupling<sup>7</sup>, that a compact trimer with antiferromagnetic interactions sitting on the surface suffer necessarily magnetic frustration. This leads to the well-known non-collinear Neel states being characterized by 120° angles between the moments. Hence, we face in such a system an interplay between the non-collinear coupling tendencies arising from the interaction among the adatoms in the cluster and the collinear tendencies arising from the additional coupling to the substrate atoms: this is very different to the Ni(001) surface where the frustration arises from the competition between the coupling in the cluster and with the substrate<sup>4</sup>.

## II. CALCULATIONAL METHOD

Our calculations are based on the Local Spin Density Approximation (LSDA) of density functional theory with the parametrization of Vosko *et al.*<sup>12</sup>. The full non-spherical potential was used, taking into account the correct description of the Wigner-Seitz atomic cells.<sup>13,14</sup> Angular momenta up to  $l_{\max} = 3$  were included in the expansion of the Green functions and up to  $2l_{\max} = 6$  in the charge density expansion. Relativistic effects were described in the scalar relativistic approximation.

First, the surface Green functions are determined by the screened KKR method<sup>15</sup> for the (111) surface of Ni which serves as the reference system. The LSDA equilibrium lattice parameter of Ni was used (6.46 a.u.  $\approx 3.42$  Å) and the magnetic moment at the surface is  $0.63 \mu_B$ . To describe the Cr and Mn adatoms on the surface we consider a cluster of perturbed potentials with a size of 48 perturbed sites for all kind of ad-clusters considered. We consider the adatoms at the unrelaxed hollow position in the first vacuum layer. We allow for the relaxation of the magnetic moment directions with respect to the direction of the substrate magnetization<sup>4</sup>.

### III. THEORETICAL BACKGROUND

Since the collinear magnetic state represents a self-consistent solution of the Kohn-Sham equations, total energy calculations are necessary to check whether the non-collinear solution represents a true energy minimum or only a local minimum, with the collinear state representing the total minimum. This proved to be important, e.g., for Cr dimers on Ni(001)<sup>4</sup>, where the collinear solution was found to have a lower total energy.

The driving mechanism for non-collinear magnetism in small transition metal clusters is a competition of antiferromagnetic (or antiferromagnetic and ferromagnetic) interactions. In other cases, such as *f*-element systems<sup>16</sup> or ad-layers and chains<sup>17,18</sup>, the spin-orbit interaction can also be of significance but in transition metals usually frustration is the dominating effect. In the case of magnetically non-collinear transition metal clusters adsorbed on ferromagnetic surfaces, it is helpful for the interpretation of the results to distinguish between three factors contributing to the solution: (i) the magnetic interaction of the cluster adatoms with the substrate, (ii) the magnetic pair interaction among the atoms in the cluster, and (iii) the geometry of the cluster. This separation is meaningful because the first-neighbours exchange interaction is energetically dominant compared to second, third, etc. neighbours, and because in different cluster sizes or shapes the type of pair interaction (ferro- or antiferromagnetic) does not change qualitatively. Quantitatively, however, this is only an approximation, and effects beyond this are included in the self-consistent solution. In view of the above, we proceed by first presenting results for the single adatoms, then the dimers, and then trimers and tetramers of various shapes. We expect that Cr and Mn clusters are candidates for non-collinear magnetism, because the Cr-Cr and Mn-Mn first-neighbors pair interactions are antiferromagnetic.

### IV. SINGLE ADATOMS AND DIMERS

Investigating the magnetism of ad-clusters starts by understanding the magnetism of adatoms and ad-dimers.

—*Single Adatoms.* Our calculations show that the single Cr adatom is AF coupled to the surface with an increase of the magnetic moments ( $M_{AF} = 3.77 \mu_B$  and  $M_{FM} = 3.70 \mu_B$ ) compared to the results obtained for Ni(001)<sup>4</sup> ( $M_{AF} = 3.48 \mu_B$  and  $M_{FM} = 3.35 \mu_B$ ). This increase arises from the weaker hybridization of the 3d wavefunctions with the substrate—the adatom has three neighbours on the (111) surface and four on the (001). The calculated energy difference between the FM and AF configurations is high so that the AF configuration is stable at room temperature ( $\Delta E_{AF-FM} = -93.54$  meV, corresponding to 1085 K). Also our results for the Mn adatom on Ni(111) are similar to what we found on Ni(001). The single Mn adatom prefers to couple ferromagnetically to the substrate. The energy

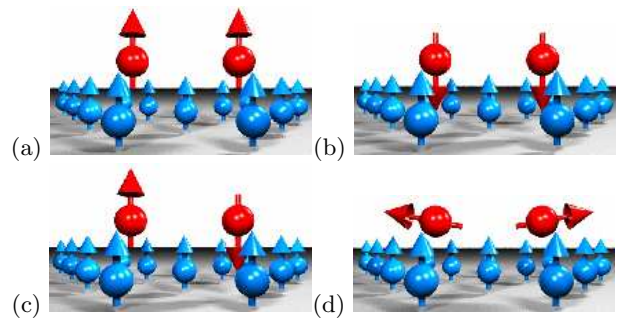


FIG. 1: Different magnetic configurations of Mn Dimer on Ni(001). The configurations correspond to FM in (a), AF in (b), Ferri in (c) which is the ground state, and the non-collinear additional local minimum in (d). See text for the discussion.

difference between the two possible magnetic configurations is  $\Delta E_{AF-FM} = 208$  meV. For the (001) surfaces the energy differences are both for Cr and Mn larger, since they roughly scale with the coordination number ( $\Delta E_{AF-FM}^{Cr} = -134$  meV,  $\Delta E_{AF-FM}^{Mn} = 252$  meV). The magnetic moments of Mn are high and reach a value of  $4.17 \mu_B$  for the FM configuration and  $4.25 \mu_B$  for the AF configuration. The moments are higher than for the Mn adatoms on Ni(001) ( $M_{AF} = 4.09 \mu_B$  and  $M_{FM} = 3.92 \mu_B$ ), again due to the lower coordination and hybridization of the 3d levels. This type of coupling to the substrate (AF for Cr and FM for Mn) can be understood in terms of the *d-d* hybridization of the adatom wavefunctions with the ones of the substrate, and is described, e.g., in Ref. 4.

—*Dimers.* For the compact dimers, three collinear configurations are possible: ferromagnetic (FM) (see fig. 1(a)), with the moments of both atoms parallel to the substrate moments (fig. 1(b)), antiferromagnetic (AF), with the moments of both atoms antiparallel to the substrate moments, and ferrimagnetic (Ferri) (see fig. 1(c)), where the magnetic moment of one of the dimer atoms is parallel to the moments of the substrate, while the other one is antiparallel. Since the direct exchange in a Cr pair (or a Mn pair) is antiferromagnetic (for an explanation in terms of the Alexander-Anderson model<sup>19</sup> see<sup>4</sup>), and stronger than the adatom-substrate interaction, the Ferri solution is expected to prevail. Indeed, Cr dimers on Ni(111) as on Ni(001) are characterized by a collinear Ferri coupling as a ground state. The difference is, however, that no non-collinear solution was found on Ni(111), as opposed to Ni(001)<sup>4</sup>. This is understandable, because the non-collinear state in the dimer on Ni(001) arises from the competition between the intradimer Cr-Cr antiferromagnetic interaction and the Cr-Ni antiferromagnetic interaction. On the Ni(111) surface, the coordination to the Ni substrate is lower, therefore the interaction with the substrate is insufficient to overcome the Cr-Cr interaction. In fact the Ferri total energy is 317.32 meV/adatom lower than the AF one and 352.54 meV/adatom lower than the FM one.

		Cr <sub>2</sub>	Mn <sub>2</sub>
AF	moments	(−3.47, −3.47)	(−4.02, −4.02)
	$E_{AF} - E_{Ferri}$	317.32	243.2
Ferri	moments	(−3.30, 3.31)	(−3.97, 3.85)
FM	moments	(3.38, 3.38)	(3.98, 3.98)
	$E_{FM} - E_{Ferri}$	352.54	76.31

TABLE I: Atomic spin moments (in  $\mu_B$ ) and energy differences (in meV) of the adatom dimers on Ni(111) in the collinear configurations. A minus sign of the collinear moments indicates an antiparallel orientation with respect to the substrate magnetization.

Dimer type:	Cr <sub>2</sub>	Cr <sub>2</sub>	Mn <sub>2</sub>	Mn <sub>2</sub>
Substrate:	Ni(111)	Ni(001)	Ni(111)	Ni(001)
$E_{FM-Ferri}$	353	451	76	65
$E_{AF-Ferri}$	317	433	243	496

TABLE II: Dimer energies (in meV/adatom) in the FM, AF, and Ferri configurations of Cr and Mn dimers on Ni(111). Results of the same dimers on Ni(001), taken from Ref. 4, are also shown for comparison.

Similar trends are found for the Mn dimers on Ni(111): The Ferri solution is the most stable collinear solution. However, in addition a non-collinear solution is found, which is only slightly higher, *i.e.* by 4.44 meV/adatom than the Ferri solution. Note that on the Ni(001) surface<sup>4</sup>, this type of dimer state, shown in fig. 1(d), represents the ground state, which is, however, not the case for the dimer on (111) preferring the Ferri configuration. In the non-collinear configuration (fig. 1(d)), both adatom moments ( $3.90 \mu_B$ ), while aligned antiferromagnetically with respect to each other, are slightly tilted in the direction of the substrate magnetization with a rotation angle of  $\theta = 79^\circ$  (instead of  $90^\circ$ ). The energy differences between the Ferri with the other local minima AF and FM are respectively 243.2 meV/adatom and 76.31 meV/adatom. The magnetic moments and energy differences are given in Table I. Note that the local Cr and Mn moments are considerably higher than the corresponding local moments in dimers on Ni(001)<sup>4</sup>, again a result of the reduced coordination number.

As we have discussed in Ref. 4, the different magnetic configurations of the Ni substrate atoms cannot be described well by the Heisenberg model, since the moments of the atoms adjacent to the adatoms are strongly reduced. Such longitudinal moment relaxations cannot be described by this model.

## V. ADATOM TRIMERS

Trimers in equilateral triangle geometry are, in the presence of antiferromagnetic interactions, prototypes for non-collinear magnetism, with the magnetic moments of

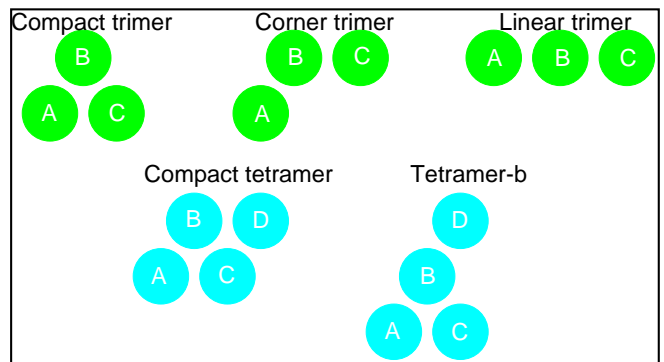


FIG. 2: Different geometrical configurations considered for trimers and tetramers at the surface of Ni(111).

the three atoms having an angle of  $120^\circ$  to each other<sup>8</sup>. This  $120^\circ$ -configuration is a well-known consequence of the magnetic frustration in such triangular systems. Examples are compact Cr or Mn trimers on (111) surfaces of noble metals (see for instance a recent calculation of  $Mn_3$  on Cu(111) reported in Ref. 7). In our case, the  $120^\circ$  state is perturbed by the exchange interaction with the substrate, and therefore the magnetic configuration is expected to be more complicated.

Let us start with a Cr dimer (Mn dimer) that we approach by a single Cr adatom (Mn adatom). As shown in Fig.2, three different types of trimers can be formed: i) the compact trimer with an equilateral shape, ii) the corner trimer with an isosceles shape and iii) the linear trimer. The adatoms are named A, B and C.

When the distance between the ad-dimer and the single adatom is large enough that their magnetic interaction is weak (second-neighboring positions<sup>4</sup>), the total moment is  $-3.78 \mu_B$  for the Cr case and  $4.05 \mu_B$  for the Mn one. Let us move the single adatom close to the dimer and form a compact trimer. The distance between the three adatoms is the same, meaning that this is a prototype geometry which leads for a trimer in free space to a  $120^\circ$  rotation angle between the magnetic moments. This is attested for the Cr case for which we had difficulties finding a collinear solution. Our striking result, as depicted in fig. 3a-b, is that the non-collinear  $120^\circ$  configuration is conserved with a slight modification. Indeed, our self-consistent  $(\theta, \phi)$ -angles are  $(2^\circ, 0^\circ)$  for adatom B and  $(126^\circ, 0^\circ)$  for adatom A and  $(122^\circ, 180^\circ)$  for adatom C. The angle between B and A is equal to the angle between B and C ( $124^\circ$ ) while the angle between A and C is  $112^\circ$ . The small variation from the prototypical  $120^\circ$  configuration is due to the additional exchange interaction with Ni atoms of the surface. Let us suppose that we start with a  $120^\circ$  configuration of a compact Cr trimer, neglecting at first the exchange interaction with the substrate. This gives an infinite number of degenerate configurations being distinguished by an arbitrary rotation of all moments in spin space. This degeneracy is (partly) removed by coupling to the substrate atoms,

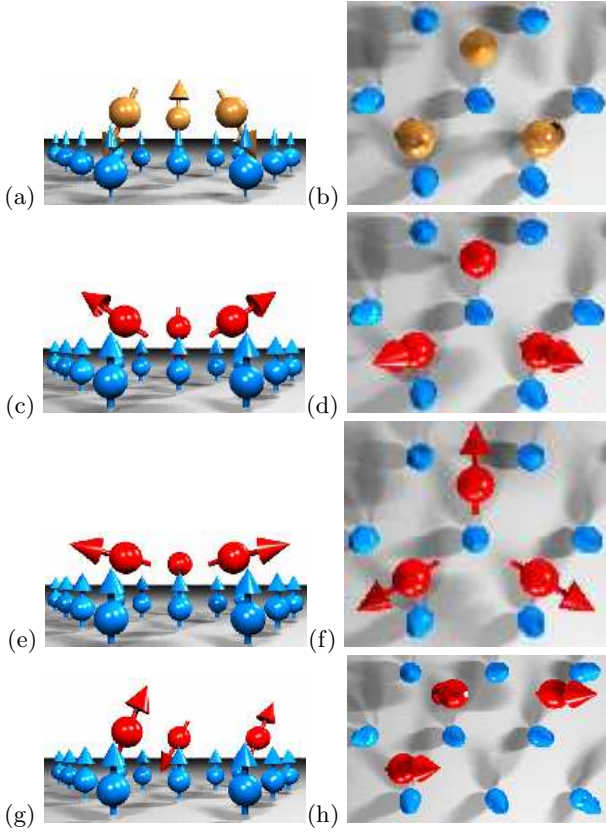


FIG. 3: Side view (a) and top view (b) are shown for the most stable configuration of Cr compact trimer on Ni(111) (in blue). (c) and (d) represent the side view and top view of the ground state (NCOL2) of Mn compact trimer on Ni(111) while (e) and (f) depict an almost degenerate state (NCOL3) of the same Mn trimer. Finally, the side view (g) and top view (h) are shown for the most stable configuration of Mn (in red) corner trimer on Ni(111). (see text for more details).

the moments of which are fixed by anisotropy, *e.g.* in [111] direction. Since the adatom-substrate interaction is AF, the moments of two adatoms rotate so that they are partly oriented opposite to the substrate magnetization, while the moment of the third adatom rotates to the opposite direction, driven by the AF interaction to its Cr neighbors. The coupling with the substrate leads thus to a deviation from the prototype  $120^\circ$  state, with an additional rotation of  $2^\circ$  for the FM adatom and of  $4^\circ$  for the two other adatoms. The ferromagnetic Cr carries a moment of  $2.94 \mu_B$ , smaller than the neighboring moments ( $3.31 \mu_B$ ). Hence, the total magnetic moment of all the adatoms is  $-0.76 \mu_B$ . Note the huge jump of the total magnetic moment (80%) from  $-3.78 \mu_B$ , which is the initial non-interacting dimer-adatom total moment.

For the compact Mn trimer, three non-collinear configurations were obtained: As in the case of the compact Cr trimer, the free Mn trimer must be in a  $120^\circ$  configuration. Nevertheless, the magnetism of the substrate changes this coupling taking into account the single

adatom behavior: Mn adatoms prefer a FM coupling to the substrate and an AF coupling with their neighboring Mn adatom. The first non-collinear magnetic configuration (NCOL1) is similar to the Cr one (fig. 3a-b), *i.e.* adatom B couples FM ( $3.61 \mu_B$ ) with the substrate moments while adatom A ( $3.67 \mu_B$ ) and C ( $3.67 \mu_B$ ) are rotated into the opposite direction with an angle of  $114^\circ$  between B and A and between B and C (see Table III). The second non-collinear configuration (NCOL2) has the opposite magnetic picture (fig. 3c-d) as compared to compact Cr trimer *i.e.*: there is a rotation of the moment of atom B ( $3.70 \mu_B$ ) to an almost AF coupling ( $\theta = 179^\circ$ ,  $\phi = 0^\circ$ ) forced by the two other adatoms (A and C) which tend to couple FM to the substrate by experiencing an additional rotation angle of  $10^\circ$  towards a FM coupling *i.e.* atom A carries a moment of  $3.62 \mu_B$  rotated by ( $\theta = 49^\circ$ ,  $\phi = 0^\circ$ ) instead of ( $\theta = 60^\circ$ ,  $\phi = 0^\circ$ ) which characterize the free Mn trimer. On the other hand, atom B has a moment of  $3.62 \mu_B$  rotated by ( $\theta = 51^\circ$ ,  $\phi = 180^\circ$ ). The angle between B and A is equal to the angle between B and C ( $50^\circ$ ) while the angle between A and C is  $260^\circ$ . In the third magnetic configuration (NCOL3) the three moments ( $3.65 \mu_B$ ) are almost in-plane and perpendicular to the substrate magnetization (see fig. 3e-f). They are also slightly tilted in the direction of the substrate magnetization ( $\theta = 86^\circ$ ) due to the weak FM interaction with the Ni surface atoms. Within this configuration, the  $120^\circ$  angle between the adatoms is kept. Total energy calculations show that the NCOL2 configuration is the ground state which is almost degenerate with NCOL1 and NCOL3 ( $\Delta E_{\text{NCOL1-NCOL2}} = 1.27 \text{ meV/adatom}$  and  $\Delta E_{\text{NCOL3-NCOL2}} = 5.61 \text{ meV/adatom}$ ). Thus already at low temperatures trimers might be found in all three configurations; in fact the spin arrangement might fluctuate between these three  $120^\circ$  configurations or even at low temperatures, between the three degenerate configurations of the NCOL1 or the NCOL2 state. Compared to the collinear state energy of the compact trimer, the NCOL2 energy is lower by  $138.23 \text{ meV/adatom}$ . This very high energy difference is due to frustration, even higher than breaking a bond as shown in the next paragraphs. Contrary to this, the corner trimer shows no frustration which leads to a collinear ground state. For instance, the total moment of the non-collinear compact trimer ( $0.95 \mu_B$ ) experiences a decrease of 76% compared to the obtained value for the non-interacting dimer-adatom configuration.

The next step is to move the additional adatom C and increase its distance with respect to A in order to reshape the trimer into an isosceles triangle (what we call “corner trimer” in fig. 2, with one angle of  $120^\circ$  and two of  $30^\circ$ ). By doing this, the trimer loses the frustration and is characterized, thus, by a collinear ferrimagnetic ground state: the moments of adatoms A and C are AF oriented to the substrate (following the AF Ni-Cr exchange), while the moment of the central adatom B is FM oriented to the substrate, following the AF Cr-Cr coupling to its two neighbors. The magnetic moments



Noncol. config.	Adatom	Moment ( $\mu_B$ )	$\theta$ (deg)	$\phi$ (deg)
NCOL1	A	3.67	115	0
	B	3.61	1	0
	C	3.67	113	180
NCOL2	A	3.62	49	0
	B	3.70	179	0
	C	3.62	50	180
NCOL3	A	3.65	86	120
	B	3.65	86	0
	C	3.65	86	120

TABLE III: Atomic moments and rotation angles of the magnetic moments of Mn adatoms forming a compact trimer on Ni(111) surface. For the adatom notation see fig. 2.

do not change much compared to the compact trimer. The central adatom B carries a moment of  $2.94 \mu_B$  while the two others have a slightly more sizeable moment of  $-3.32 \mu_B$ . Thus, the total magnetic moment ( $-3.70 \mu_B$ ) increases to a value close to the one obtained for non-interacting dimer-adatom system.

While the non-collinear state is lost for the corner Cr trimer, it is present for the corner Mn trimer as a local minimum with a tiny energy difference of 4.82 meV/adatom higher than the Ferri ground state. This value is equivalent to a temperature of  $\sim 56$  K, meaning that at room temperature both configurations co-exist. Here Ferri means that the central adatom B is AF oriented to the substrate with a magnetic moment of  $3.71 \mu_B$ , forced by its two FM companions A and C (moment of  $3.83 \mu_B$ ) which have only one first neighboring adatom and are less constrained. The total moment of the ad-cluster is also high ( $3.95 \mu_B$ ) compared to the compact trimer value, reaching the value of the non-interacting system (with the third atom of the trimer far away from the other two).

The Ferri solution is just an extrapolation of the non-collinear solution shown in fig. 3g-h (with magnetic moments similar to the collinear ones) in which the central adatom B ( $3.70 \mu_B$ ) tends to orient its moment also AF to the substrate ( $\theta = 152^\circ$ ,  $\phi = 0^\circ$ ) and the two other adatoms with moments of  $3.83 \mu_B$  tend to couple FM to the surface magnetization with the same angles ( $\theta = 23^\circ$ ,  $\phi = 180^\circ$ ). It is important to point out that the AF coupling between these two latter adatoms is lost by increasing the distance between them. Indeed, one sees in fig. 3g-h that the two moments are parallel. The total magnetic moment is also high and is equal to  $3.78 \mu_B$ .

Let us move furthermore adatom C in order to form a linear trimer. For the Cr case, there is no non-collinear magnetism. The already stable Ferri solution for the corner trimer is comforted. The moments of the adatoms A and C are a bit higher than what obtained so far for the other structural configuration, *i.e.*, adatoms A and C have a moment of  $-3.40 \mu_B$  while the central moment is equal to  $2.97 \mu_B$ : the coupling between A and C is

now indirect (through the central adatom). The total magnetic moment is also high ( $-3.83 \mu_B$ ).

Concerning the Mn case for a chain, a non-collinear configuration was obtained as a local minimum with a small energy difference compared to the ground state which is the collinear Ferri solution (8.50 meV/adatom  $\sim 98.64$  K). The magnetic moments do not change a lot compared to the values obtained for the corner trimer. The central adatom B carries a moment of  $-3.78 \mu_B$  while the A and C have a higher moment of  $3.84 \mu_B$ . In the non-collinear solution, the central Mn adatom with a moment of  $3.76 \mu_B$ , as seen previously, tends to couple AF with ( $\theta = 142^\circ$ ,  $\phi = 0^\circ$ ) and the A and C with a similar moment of  $3.85 \mu_B$  tend to couple FM to the substrate ( $\theta = 28^\circ$ ,  $\phi = 180^\circ$ ). The total moment is high for both magnetic configurations. For the Ferri solution, it reaches  $3.90 \mu_B$ , while for the non-collinear solution the total moment value is smaller ( $3.84 \mu_B$ ).

It is interesting to compare the total energies of the three trimers we investigated. The compact trimer has more first neighboring bonds and is expected to be the most stable trimer. The energy differences confirm this statement. Indeed the total energy of the Cr compact trimer is 119 meV/adatom lower than the total energy of the corner trimer and 198.16 meV/adatom lower than the total energy of the linear trimer. Similarly, the Mn compact trimer has a lower energy of 53 meV/adatom compared to the corner trimer and a lower energy of 100 meV/adatom than the linear trimer.

By summarizing the results for the total moments of the adatoms, we see that the non-interacting cluster consisting of a single adatom and an adatom dimer has a high moment. This large total moment also survives for linear and corner trimers. However the most stable compact trimer has a low moment,  $0.95 \mu_B$  in the case of Mn and  $-0.76 \mu_B$  for Cr.

## VI. ADATOM TETRAMERS

We consider two types of tetramers, formed by adding a Cr or Mn adatom (atom D in fig. 2) to the compact trimer. We begin with the compact tetramer (see fig. 2 and fig. 4a-b). For both elements Cr and Mn, the Ferri solution is the ground state (fig. 4a). For Cr (Mn) compact tetramer, the A and D adatoms are FM oriented to the surface atoms with a moment of  $2.31 \mu_B$  ( $3.60 \mu_B$ ) while B and C are AF oriented to the substrate with a moment of  $2.87 \mu_B$  ( $3.43 \mu_B$ ). This gives a magnetic configuration with a low total magnetic moments of  $-1.12 \mu_B$  for Cr tetramer and  $0.34 \mu_B$  for Mn tetramer. The Cr tetramer, in particular, shows also a non-collinear configuration (fig. 4b) as a local minimum which has, however, a slightly higher energy of  $\Delta E_{\text{NCOL-Ferri}} = 1$  meV/adatom. Within this configuration the AF coupling between the adatoms is observed. However, the four moments are almost in-plane perpendicular to the substrate magnetization. The tilting is small ( $\theta = 93^\circ$ ) due to the

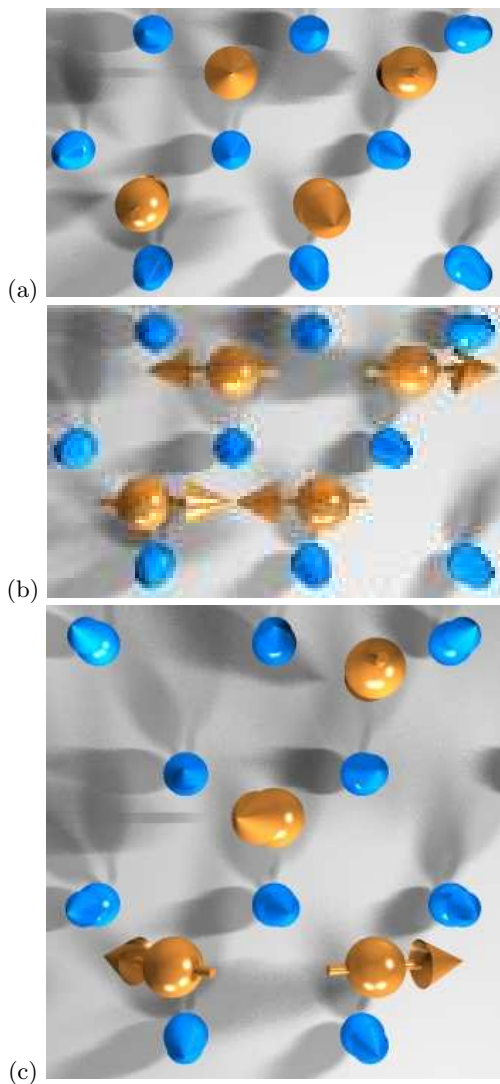


FIG. 4: Top view of the collinear most stable solution (a) and the non-collinear metastable configuration (b) of compact Cr tetramer on Ni(111). In (c) is depicted The Cr tetramer-b magnetic ground state on Ni(111), which basically consists of the non-collinear trimer state of fig.3a coupled antiferromagnetically to the fourth adatom.

weak AF coupling with the substrate.

An additional manipulation consists in moving the adatom D and forming a tetramer-b (fig. 4c). For such a structure, the collinear solution for the Cr tetramer is only a local minimum. In this structure, atom D has less neighboring adatoms compared to A, B, and C. In the non-collinear solution which is the magnetic ground state, the moment of adatom D ( $3.34 \mu_B$ ) is almost AF oriented to the substrate ( $\theta = 178^\circ$ ,  $\phi = 0^\circ$ ). The remaining adatoms form a compact trimer in which the closest adatom to D, *i.e.* B, tends to orient its moment FM ( $2.45 \mu_B$ ) to the substrate ( $\theta = 19^\circ$ ,  $\phi = 0^\circ$ ) while the moments of A ( $2.90 \mu_B$ ) and C ( $2.80 \mu_B$ ) tend to be oriented AF ( $\theta_A = 124^\circ$ ,  $\phi_A = 0^\circ$ ) and ( $\theta_C = 107^\circ$ ,  $\phi_C$

$= 180^\circ$ ). In the (metastable) collinear solution for this tetramer, the moment of adatom B is oriented FM to the substrate while the moments of all remaining adatoms are oriented AF to the surface atoms. Here, the total magnetic moment has a high value of  $-3.46 \mu_B$ . The total energy difference between the two configurations is equal to 49.32 meV/adatom. Compared to the total energy of the compact tetramer, our calculations indicate that the tetramer-b has a higher energy (108.72 meV/adatom).

Let us now turn to the case of the Mn tetramer-b. Also here, the non-collinear solution is the ground state while the collinear one is a local minimum. The energy difference between the two solutions is very small (2.82 meV/adatom). The moments are now rotated to the opposite direction compared to the Cr case, in order to fulfill the magnetic tendency of the single Mn adatom which is FM to the substrate. The Mn atom with less neighboring adatoms, *i.e.* D, has a moment of  $3.84 \mu_B$  rotated by ( $\theta = 27^\circ$ ,  $\phi = 0^\circ$ ), while its closest neighbor, the atom B with a moment of  $3.44 \mu_B$ , is forced by the neighboring companions to couple AF ( $\theta = 140^\circ$ ,  $\phi = 180^\circ$ ). The adatoms A and C with similar magnetic moments ( $3.63 \mu_B$ ) tend to couple FM with the following angles: ( $\theta = 81^\circ$ ,  $\phi = 0^\circ$ ) and ( $\theta = 34^\circ$ ,  $\phi = 0^\circ$ ). As in the case of Cr tetramer-b, the converged collinear solution is just the extreme extension of the non-collinear one: The “central” adatom of the tetramer is forced by its FM Mn neighboring atoms to coupled AF to the substrate. The magnetic regime is similar to the one of Cr tetramer-b, *i.e.* high, with a total magnetic moment of  $4.37 \mu_B$ .

As expected, the most stable tetramer is the compact one, with an energy of 52.26 meV/adatom lower than tetramer b.

## VII. SUMMARY

As a summary, we have investigated the complex magnetism of small Cr and Mn ad-clusters on Ni(111). This is a prototype system where two types of magnetic frustration occur: (i) frustration within the ad-cluster and (ii) frustration arising from antiferromagnetic coupling between the adatoms in the cluster and competing magnetic interaction between the adclusters and the surface atoms. While the resulting collinear and non-collinear structures are very complex, a unifying feature is that all compact structures (dimers, trimers and tetramers) have very small total moments, as a result of the strong antiferromagnetic coupling between the cluster atoms leading to a nearly complete compensation of the local moments, while the more open structures, like the corner and linear trimers and the tetramer b, have rather large total moments of about  $4 \mu_B$ . Since the transition between a compact and an open structure requires to move one adatom by just one atomic step, we might consider this motion as a magnetic switch, which via the local magnetic exchange field of the single adatom allows to switch

the total moment on and off, and which therefore might be of interest for magnetic storage. Thus magnetic frustration might be useful for future nanosize information storage.

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